

Chemical Composition of Fine Particles in the Tennessee Valley Region and Its Relationship to Stationary Sources

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EXTENDED ABSTRACT

As the monitoring and regulatory implementation schedules for the revised particulate matter (PM) National Ambient Air Quality Standard (NAAQS) evolve, it is clear that the new annual NAAQS metric for fine particulate matter with aerodynamic diameter less than $2.5\ \mu\text{m}$ ($\text{PM}_{2.5}$) will be difficult for many parts of the country to attain. The need to better understand the composition of fine particles ($\text{PM}_{2.5}$) and its temporal and spatial variability is broadly supported within regulatory, industrial and research communities. Realizing the potential consequences of the revised PM NAAQS, the Tennessee Valley Authority (TVA) and Tennessee Valley state and local regulatory organizations began operating the first comprehensive, regional prototype-FRM $\text{PM}_{2.5}$ monitoring network in the eastern U.S. on April 22, 1997^{1,2}. Every third-day $\text{PM}_{2.5}$ sampling was initiated at three core sampling stations in Nashville, Knoxville, and Lawrence County, TN. Five additional sites were added in Chattanooga and Memphis TN (August 1997), Decatur AL and Paducah KY (October 1997), and Huntsville, AL (June 1998).

The single-event particulate matter sampler models used in this effort included five prototype Partisol®-FRM Model 2000 (R&P Inc.) samplers, three prototype RAAS™ Model 2.5-100 (Graseby-Andersen) samplers, and one EPA-designated FRM $\text{PM}_{2.5}$ sampler, Model PQ200 (BGI Inc.). Each of these samplers draw air through a 10 micron (μm) size-selective inlet and remove particles greater than $2.5\ \mu\text{m}$ with a WINS impactor. The $\text{PM}_{2.5}$ particles themselves were collected on Zeflur™ Teflon 46.2-mm filters with 2 mm pore size (Gelman Sciences, Inc.) through December 1998, thereafter on ID-stamped, Whatman filters with support rings. Initially, samples were collected for a 24-hour period every third-day; the sampling frequency was changed to every sixth-day on October 1, 1998.

Following gravimetric analysis (Mettler Microbalance), selected 24-hour samples were analyzed for elements Al through Pb using x-ray fluorescence (XRF) by EPA-approved Protocol 3. After XRF analysis, the samples were extracted ultrasonically and analyzed by the TVA's Support Services Group for ammonium by automated indophenol colorimetry and for sulfate and nitrate by ion chromatography. For selected sampling days at the network's core sites, samples of fine mass were collected on collocated samplers using quartz as the collection medium. These quartz filters were analyzed by the thermo-optical reflectance (TOR) technique³ for organic and elemental carbon. The filters were then extracted ultrasonically in water and analyzed for ammonium, sulfate, and nitrate as described above for Teflon filters. Data from the collocated Teflon & quartz samples were used to determine the average chemical composition of fine particles by season at the three core sites. Specific attention was given to seasonal variations in the fine particle chemical composition, and in composition differences between urban and rural sites.

During two additional periods, more intensive sampling was done at a mobile-source impacted site in Chattanooga, TN, about 3 km from the network site. Continuous measurements of mass (TEOM) and light scattering ($3\text{-}\lambda$ nephelometer) were made in early March, 1998, and repeated, with the addition of continuous elemental carbon measurements (aethalometer⁴), in September, 1998. The data from these measurements were used to examine diurnal and seasonal variations in mass and composition at this site. A new sampler (PC-BOSS⁵) designed to accurately measure both non-volatile and semi-volatile constituents of fine mass was tested at urban and rural sites to test the accuracy of the prototype FRMs. Our ongoing assessment of data from network and special studies allow us to provide preliminary answers to the following questions.

- *What are the fine particle mass concentrations in the South-central US and what are the implications relative to the NAAQS?* Fine particle annual mass concentrations in the Tennessee Valley range from 14 to 20 micrograms per cubic meter ($\mu\text{g}/\text{m}^3$). All seven urban/suburban sites exceeded the $15\ \mu\text{g}/\text{m}^3$ level of the annual $\text{PM}_{2.5}$ standard. The rural Lawrence County TN site remained below the annual standard (Table). None of the stations exceeded the $65\ \mu\text{g}/\text{m}^3$ level of the 24-hour $\text{PM}_{2.5}$ standard. Summer high-winter low seasonality is evident.

• *How well does the Federal FRM measure fine mass and what positive and negative biases does it have?* The current FRM PM_{2.5} mass measurements underestimate the contribution of volatile/semi-volatile nitrates and organic carbon species. Preliminary information from the summer of 1997 (PC-BOSS sampler) at our Lawrence County site indicates that the semi-volatile fraction is both highly variable and significant⁶. Since the organic fraction of fine particles appears to be highly suspect from a health effects standpoint, it is prudent to make periodic assessments of semi-volatile and non-volatile organic carbon fractions when particle composition measurements are made.

• *What is the composition of these fine particles and what do they imply for development of control strategies?* Based on composition measurements, both inorganic sulfate and carbonaceous compounds make up large fractions of PM_{2.5} mass (Figure). Sulfate provides the largest fraction (≈50%) in background air (Lawrence County) with organic carbon compounds making up next largest fraction (≈33%). For the urban stations the situation is largely reversed with the organic aerosol fraction being dominant (≈50%) followed by sulfate (≈30%). Control strategies designed to lower organic carbon (transportation and industrial sources) and sulfur dioxide emissions (fossil fuel combustion sources) will therefore be most effective in achieving compliance with the PM_{2.5} annual NAAQS.

• *What are the spatial, seasonal, and diurnal variations in these concentrations and what does this tell us about sources and fates?* Higher fractions of sulfate are found in fine particles at all sites in the summer months, compared to the remainder of the year. Diurnal variations show the effects of primary sources and meteorology, with higher concentrations of primary particles (e.g., elemental carbon) during the morning rush hour and higher concentrations of all constituents at the surface during periods in which a stable surface layer is present (poor vertical mixing).

• *What are the controllable fractions of fine mass and what are the sources of those potentially controllable fractions?* The largest fractions of fine mass are attributable to organic carbonaceous material and ammonium sulfates. The sulfate fraction can in theory be controlled by further reducing emissions of its gaseous precursor, SO₂, although non-linear gas-to-particle conversion processes appear to be reducing the "bang for the buck". The organic fraction is largely uncharacterized and a high priority should be placed on characterizing what fraction of it is controllable by reducing man-made emissions of particulate organics and their gas-phase precursors.

Table Monthly Mean PM_{2.5} Mass Concentrations (µg/m³). TN Valley PM_{2.5} Network

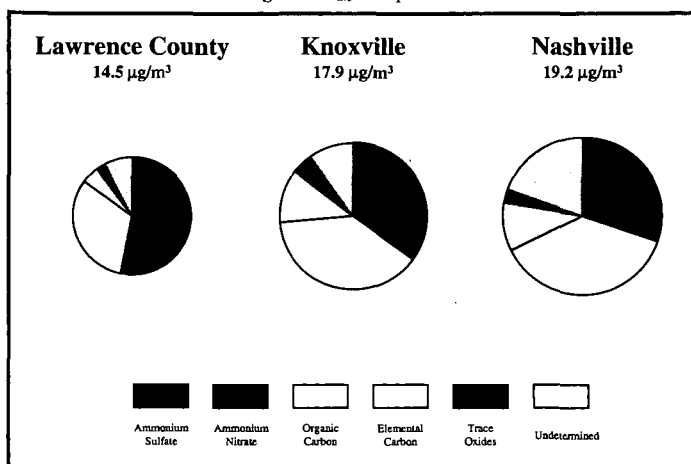
Month/Station	LC	KN	NS	CH	MP	DC	PD	HV	Mean
May-97	8.9	14.8	12.9						12.2
Jun-97	14.3	15.8	20.8						17.0
Jul-97	21.8	23.7	23.7						23.1
Aug-97	15.8	19.9	22.0	22.5					20.1
Sep-97	18.1	20.6	21.7	23.2	19.1				20.6
Oct-97	13.8	15.8	19.1	24.6	16.9	18.8	16.8		18.0
Nov-97	13.2	20.1	18.0	19.9	15.6				17.4
Dec-97	13.7	19.2	20.8	21.9	17.7	23.3	18.1		19.3
Jan-98	9.8	17.5	12.4	16.6	13.3		14.1		14.0
Feb-98	12.4	9.6	17.6	15.7	22.6		16.6		15.7
Mar-98	11.4	10.0	16.3	14.4	15.4	15.6	13.0		13.7
Apr-98	14.0	13.8	16.3	16.2	16.0	22.9	15.0		16.3
May-98	16.9	26.8	22.7	24.7	26.0	22.4	23.2		23.2
Jun-98	13.8	14.5	16.4	16.9	18.8	23.7	15.6		17.1
Jul-98	15.6	22.5	22.0	22.2	18.1	24.8	24.3	24.6	21.8
Aug-98	22.7	25.4	32.8	30.3	22.0	22.4	31.8	24.8	26.5
Sep-98	18.5	23.1	21.8	26.4	20.8		19.3	19.6	21.3
Oct-98	10.5	11.8	17.2	14.9	10.5		10.6	14.4	12.8
Nov-98	15.9	16.5	16.9	26.2	15.1		23.9	20.5	19.3
Dec-98	8.3	12.9	12.5	10.6	10.7		11.2	10.6	11.0
Jan-99	10.3	12.3	13.7	13.7	9.7		13.0	11.8	12.1
Feb-99	11.3	13.4	15.1	16.3	11.5		14.7	14.3	13.8
Mar-99	8.8		13.1	13.1	9.5		14.6	11.3	11.7
Apr-99	9.7		10.8	12.9			11.7	10.3	11.1
May-99	13.9			20.2			12.5	13.5	15.0
Jun-99	15.0			22.2			22.2	15.3	18.7
Station Mean	13.8	17.3	18.2	19.4	16.3	21.7	17.1	15.9	17.0

LC=Lawrence County TN, KN=Knoxville TN, NS=Nashville TN, CH=Chattanooga TN, MP=Memphis TN, DC=Decatur AL, PD=Paducah KY, HV=Huntsville AL.

Conclusions

TVA has measured fine particles ($PM_{2.5}$) in the Tennessee Valley region using prototype Federal Reference Method (FRM) samplers since April, 1997, and results indicate that compliance with the new NAAQS annual standard will be difficult. The chemical composition of fine particle samples has been estimated, and our results indicate that about 1/3 of the measured mass is sulfate, 1/3 is organic species, and the remainder is "other". The sulfate fraction is highest at rural sites and during summer months, with uniformly large fractions of organic aerosol in urban areas. Short-term variability of fine particle mass has been measured, and sampling performed which accounts for semi-volatile constituents of fine mass (nitrates, organics). Results show diurnal variability affecting exposure, and suggest that FRM measurements significantly underestimate organic constituents. Potentially controllable anthropogenic sources of fine particulate organics remain largely uncharacterized.

Figure $PM_{2.5}$ Composition



References

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